

Optimization of an anode for arsenic(V) extraction

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Received: 19 May 2012 / Accepted: 22 July 2012 / Published online: 2 August 2012
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Abstract Electrochemical methods has led to the preparation of a poly(pyrrole)-modified steel electrode (SS/PPy) for testing and optimizing the polymer doping/undoping process for arsenic(V) removal. Potentiodynamic (cyclic voltammetry) electropolymerization optimal range was between -0.200 and 0.980 V vs SCE. On the other hand, the potentiostatic optimal working potential was 0.980 V. SS/PPy-modified electrode prepared under either of these optimum conditions displayed a doping/undoping process occurring at 0.700 and -0.200 V, respectively. Hence, As(V) extraction or removal was performed by incorporating the cation to SS/PPy applying a 0.700 V constant potential. Then, As(V) doped SS/PPy was transferred to another cell, in which the undoping potential (-0.200 V) was applied to remove the ion from the polymer matrix, completing thus the extraction cycle (EC). This way, for instance, with a SS of 10 cm^2 geometric area and potentiostatic deposition carried out for 10 min, arsenic removal rates over 77 % were attained for 10 EC of 60 s each. This outcome allows predicting a promising future for the method as As(V) extractor from aqueous solutions. Furthermore, the modified electrode exhibited acceptable conditions for developing a likely arsenic sensor, since a linear current vs As(V) concentration relationship exists, at least in the order of concentrations used herein (50–500 ppm).

Keywords Polypyrrole · Modified electrodes · Arsenic · Arsenic removal · Arsenic sensor

1 Introduction

Arsenic, as an element, occurs naturally in the earth's crust along with various minerals, mainly copper, sulfides, and gold [1]. Due to increasing mineral exploitation [2], this has been released and spread over the earth's surface, being an important worldwide polluting byproduct. This is the reason why it is so necessary its disposal, avoiding thus natural and human population contamination.

Arsenic can occur in four oxidation states, namely -3 , 0 , $+3$, $+5$. Arsenic is found naturally in diverse forms, some of which include a variety of acids, e.g., H_3AsO_3 , $\text{H}_3\text{AsO}_3^{2-}$, H_3AsO_4 , etc., besides arsenates, arsenites, arsine, etc. From all possible combinations of this element, pentavalent arsenic compounds are mostly highly toxic [3].

Some of the technologies used in quantitative or qualitative removal of trivalent and pentavalent arsenic involve chemical oxidation or reduction [4], from trivalent to pentavalent or vice versa, not with the purpose of removing arsenic from the environment, but to get the following oxidation state to eliminate it later by other chemical or physical methods. For instance, Rivas et al. proposed the use of nano-composites [5] and polymeric matrices [6, 7] that enable in situ As(III) electrocatalytic oxidation to As(V). Subsequently, the latter was extracted in aqueous medium through an electrostatic interaction with different ammonium derivatives. Industrial arsenic removal is accomplished by coagulation and/or electrocoagulation based on the ability of different arsenic compound to interact with certain chemicals, remaining as sediment or sludge [8, 9]. The main disadvantage of this procedure is its

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non-selective separation of the ions that are both left in the mud [8].

In this study, a way to extract and recover pentavalent arsenic using electrochemical methods, taking advantage of conducting polymers doping/undoping [10, 11], was proposed and studied. This feature has already been widely discussed by Miller et al. [12, 13], who studied and verified the existence of ferricyanide ions, $\text{Fe}(\text{CN})_6^{3-}$, incorporation by applying doping to a PPy matrix. Therefore, this information allowed postulating the electro-obtention of a poly(pyrrole)-modified steel electrode (SS/PPy) that will be used to transfer As(V) cation from one cell to another. To this end, electrochemical disturbances will be also applied [14, 15], as described in experimental.

Finally, considering that electrochemical methods are cheap and easy to implement on industrial scale, this study aims chiefly to analyze the parameters to be optimized [16] so that As(V) extraction and subsequent recovery can be efficiently performed utilizing solely electrochemical techniques.

2 Experimental

All solutions were prepared with freshly deionized water using a Heal Force (Smart Series) water purification system. The measurements were conducted in a three-compartment electrochemical cell at room temperature (20 °C) under argon atmosphere. The working electrode was an AISI 316 steel sheet, ca. 10 cm² geometric area. A Pt wire coil was the counter electrode and, as a reference electrode, an Ag|AgCl in tetramethylammonium chloride, adjusted to match the potential of a saturated calomel electrode at room temperature (20 °C) [17], was utilized.

PPy coating to obtain the modified electrode was performed using a PGSTAT-20 potentiostat applying potentiodynamic perturbations (successive cyclic voltammetric scans, CV). This procedure enables characterizing and, particularly, to establish the oxidation potential for the potentiostatic obtention of the film, in order to optimize the electropolymerization process with regard to doping/undoping of the modified electrode.

The optimum conditions for SS/PPy [18] preparation were as follows. For CV, 10 mmol L⁻¹ Py (98 %, Aldrich), 50 mmol L⁻¹ Na₂SO₄ (Merck), adjusted to pH 1.5 with

concentrated sulfuric acid (95–98 % pa, Merck), working solution; potential window between -0.200 and 0.980 V, and scan rate 50 mV s⁻¹ were utilized. As for potentiostatic work, 0.980 V during 10 and/or 20 min was used. Various salts were tested as supporting electrolyte in order to optimize film porosity. Thus, with smaller anions, the doping/undoping charge was very small and the amount of As(V) incorporated into the matrix was very low, while with larger anions a greater amount of charge was obtained. However, this was ascribed not to a greater amount of As(V) but to other species extracted as well, e.g., a large amount of bisulfate anion (HSO_4^-) that may even change the pH of the medium, losing thus reproducibility. Consequently, the same electrolytic medium to be used later on with As(V) was employed, as it turned out to be the most suitable for subsequent extractions.

SS/PPy electrochemical response was evaluated in supporting electrolyte solution until a steady doping/undoping profile was attained.

For the extraction process, consisting of successive extraction cycles (ECs), to be detailed below on the basis of Scheme 1, a 226 ppm AsO_4^{3-} (pa, Merck) solution was utilized. Doping/undoping potentials of 0.700 and -0.200 V, respectively, were used. All arsenic concentrations were obtained by atomic absorption spectrometry on a G.B.C. 902 atomic absorption spectrophotometer equipped with a HG 3,000 Hydride Generator.

3 Results and discussion

3.1 Preparation of the SS/PPy-modified electrode

The optimum potential window for SS/PPy-modified electrode preparation was obtained by CV. The anodic potential limit was near to 1.00 V, since it is known that the optimum oxidation potential fluctuates around this value [15]. The exact potential is obtained by decreasing 20 mV the oxidation potential limit of each assay (from 1.000 to 0.920 V). It was verified that increasing the potential from 0.920 to 1.000 V, the maximum current decreases, except for the 0.920 V, which presents the lowest value, being thus discarded. Finally, the most suitable anodic potential limit was determined by conducting tests to study the

Scheme 1 Schematic representation of As(V) extraction, EC, with the SS/PPy modified electrode

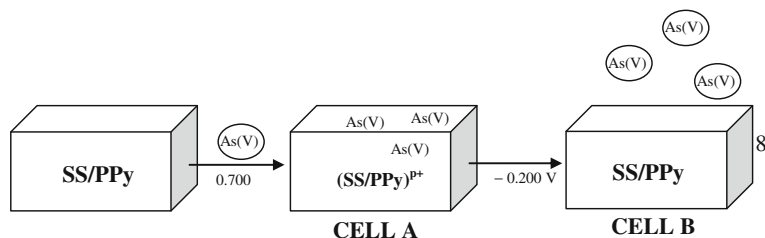


Table 1 Doping/undoping charge for obtaining anodic potential limit

Potential window (V)	Doping charge at 0.700 V (C)	Undoping charge at −0.200 V (C)
0.000–0.920	0.020	−0.016
0.000–0.940	0.024	−0.019
0.000–0.960	0.029	−0.021
0.000–0.980	0.026	−0.021

response of the polymer-modified electrode in a 100 ppm arsenic solution, searching for the doping/undoping process that in the presence of arsenate ion presents the maximum possible reversibility. The results are summarized in Table 1.

As seen in Table 1, the polymer prepared by CV in the potential range 0.000–0.980 V represents the most reversible process. Hence, 0.980 V was chosen as the more suitable anodic potential for Py electro-polymerization. Furthermore, working under the same concentration and scan-rate potential conditions, it was verified that ca. −0.500 V was the most suitable cathodic potential limit.

To determine the exact potential for maximum current, the cathodic limit variation from −0.500 to 1.000 V was studied, and −0.200 V was found to be the optimum cathodic potential limit. Consequently, the selected CV working potential window was between −0.200 and 1.000 V.

In summary, the optimal conditions for SS/PPy electro-preparation were as follows. CV sweep between −0.200 and 0.980 V, at 50 mV s^{−1} of a 10 mmol L^{−1} Py + 50 mmol L^{−1} Na₂SO₄, pH 1.5, solution.

3.2 Optimization of SS/PPy

3.2.1 Doping/undoping potentials

To optimize the doping/undoping potential pairs, comparison of the charge storage capacity (SC) [19] using potentiostatic method (PM), with two potential pairs, namely (P_1) 0.700 and −0.200 and (P_2) 0.600 and −0.200 V, was carried out. Figure 1a, revealed that the P_1 potential pair produced higher currents, both anodic and cathodic, ascribed to its higher SC. On the other hand, in Fig. 1b six successive ECs using PM between the same potential pairs of Fig. 1a were compared. It was found that P_1 potentials also allowed obtaining higher charge for each EC.

Table 2 shows a summary of the charge and theoretical percentage related to each doping/undoping cycle in Fig. 1b. In both cases the extraction percentage decreases, which is attributed to electroactivity loss after each EC, directly associated to SC decrease. However, the potential pair 0.700/−0.200 V shows ~25 % species retention into its polymeric matrix vs ~35 % species retention of pair

P_2 , demonstrating that P_1 is the most suitable pair to fulfill our goal.

Table 3 specifies SC percentage loss between two successive EC, using Table 2 doping/undoping data. It is seen that for both doping/undoping potential pairs under survey, high reversibility exists in the same EC; however, the doping value of each measurement is still greater than the undoping one.

Based on these results, P_1 was chosen since the percentage loss for each EC was ~6 % (100–94 %), while for P_2 was ~12 % (100–88 %).

3.2.2 PPy film thickness in SS/PPy

Another important parameter to be analyzed in the extraction process is PPy coating thickness upon the steel surface. A thicker deposit might also mean, as the polymerization time increases, a greater degree of crosslinking [20, 21] and, consequently, a more efficient extraction. In order to optimize this variable, the thickness of PPy films obtained using PM for 10, 30, and 60 min was studied. The results revealed that an increase of polymerization time, indeed increases the level of crosslinking. This fact is clearly evidenced by observing the electrode surface and is reflected in the respective charges obtained, namely 4,362, 14,076, and 18,966 C.

A greater charge would lead to postulate higher efficiency. However, studies of electrodes modified by these deposits in 100 ppm As(V) and 50 mmol L^{−1} Na₂SO₄ solutions to compare the likely selectivity trend toward both anions under the influence of film thickness, revealed that a shorter polymerization time generates a SS/PPy with higher reversibility for sulfate anion as well as an increase of the percentage of extracted arsenate. Hence, 10 min was selected as suitable to obtain PPy by potentiostatic electro-polymerization.

3.2.3 Effect of electrolyte concentration and temperature on SS/PPy obtention

Electrolyte concentration affects the proportionality relationship between charge amount of the doping/undoping processes. Therefore, a study on the variation of film response as the amount of supporting electrolyte in the mixture changes from 25 mmol L^{−1} (A) to 50 mmol L^{−1} (B) could outline the high sensitivity of PPy under various conditions. Figure 2a depicts how PPy sensitivity increases with SO₄^{2−} ion concentration. Therefore, any analytical measurement performed with PPy, should take into account the likely positive influence that the matrix effect exert on this, being very important that the deposits under survey exhibit high reversibility. Fortunately, the doping/undoping process is highly effective and can remove much of these

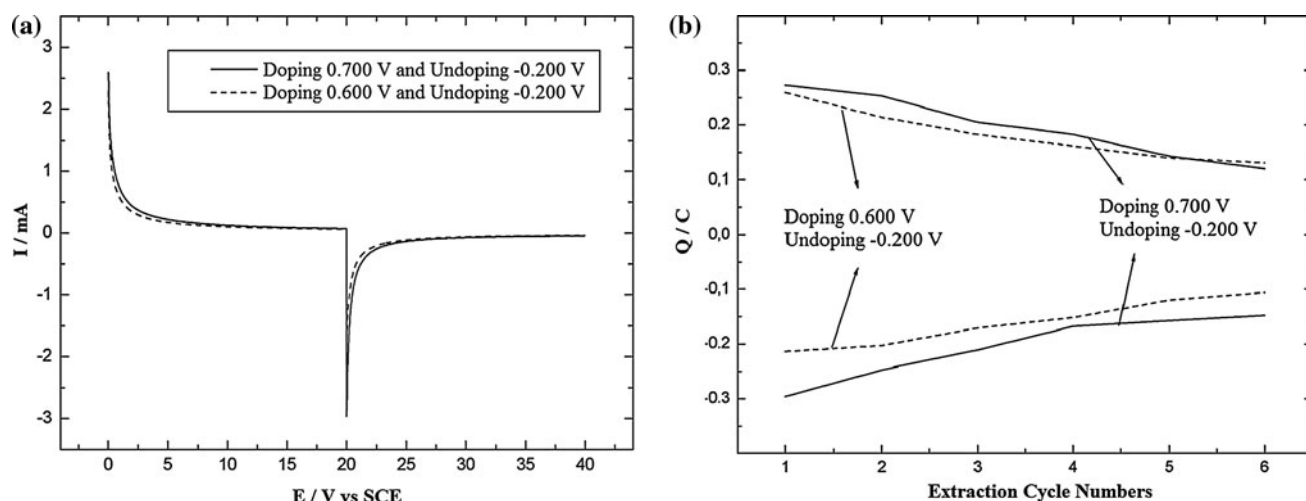


Fig. 1 **a** Comparison of SC-pair extraction potential (doping/undoping) by PM. *Doping interface*, SS/PPy/148.40 ppm As(V) + 50 mmol L⁻¹ Na₂SO₄, pH 1.5. *Undoping interface*, SS/PPy/50 mmol L⁻¹ Na₂SO₄, pH 1.5. **b** Comparison of the variation in SC by CE between

pairs of extraction potential (doping/undoping) by MP. *Doping interface*, SS/PPy/148.40 ppm As(V) + 50 mmol L⁻¹ Na₂SO₄, pH 1.5. *Undoping interface*, SS/PPy/50 mmol L⁻¹ Na₂SO₄, pH 1.5

Table 2 Comparison of charge storage capacity (SC) and the theoretical percentage of extraction working at two doping/undoping potential pairs (0.700/−0.200 and 0.600/−0.200 V)

Cycle number	1	2	3	4	5	Average	SD
Doping charge at 0.600 V (C)	0.191	0.170	0.154	0.132	0.112		
Undoping charge at −0.200 V (C)	−0.124	−0.116	−0.105	−0.085	−0.070		
% Extraction	64.92	68.23	68.18	64.01	62.59	65.59	2.53
Doping charge at 0.700 V (C)	0.527	0.479	0.448	0.426	0.406		
Undoping charge at −0.200 V (C)	−0.399	−0.373	−0.338	−0.321	−0.309		
% Extraction	75.71	77.87	75.45	75.35	76.11	76.01	1.03

Table 3 Comparative table of electro-activity loss between EC and two doping/undoping potential pairs (0.700/−0.200 V and 0.600/−0.200 V)

No. EC	Doping at 0.600 V (%)	Undoping at −0.200 V (%)	Doping at 0.700 V (%)	Undoping at −0.200 V (%)
1–2	89.00	93.54	90.89	93.48
2–3	90.58	90.52	93.53	90.62
3–4	85.71	80.48	95.09	94.97
4–5	84.85	82.95	95.31	96.26
5–6	90.17	89.30	98.02	95.46
6–7	88.06	87.36	94.55	94.16

sulfate ions from PPy by applying a potential step for a short while before using the SS/PPy device for As(V) extraction.

Temperature may also be an influential parameter in SS/PPy preparation, since an increase of the reaction kinetics sometimes allows greater thickness of deposited films due to higher crosslinking extent [22]. The assays effected herein regarding this matter, although showed that at higher

temperature a greater polymerization charge exists (Fig. 2b), demonstrated that it is indeed essential to work always at the same temperature in order to obtain accurate results [23]. Therefore, as mentioned in experimental, all work was conducted at 20 °C.

3.3 As(V) extracting process

3.3.1 Model and extraction conditions

Arsenic extraction is accomplished from solutions containing the element as arsenate ion based and using the p-doping/undoping procedure, characteristic of conductive polymers as PPy, consisting of polymer partial oxidation at the doping potential, acquiring thus positive charge. To counteract this charge, the matrix incorporates anions from the electrolyte. Then, if the process is reversible, reversing the polarity, i.e., applying the undoping potential, the polymer is reduced to its neutral form, expelling the anions (Scheme 1).

In this case to accomplish the proposed method 100 ppm As(V) + supporting electrolyte solution was

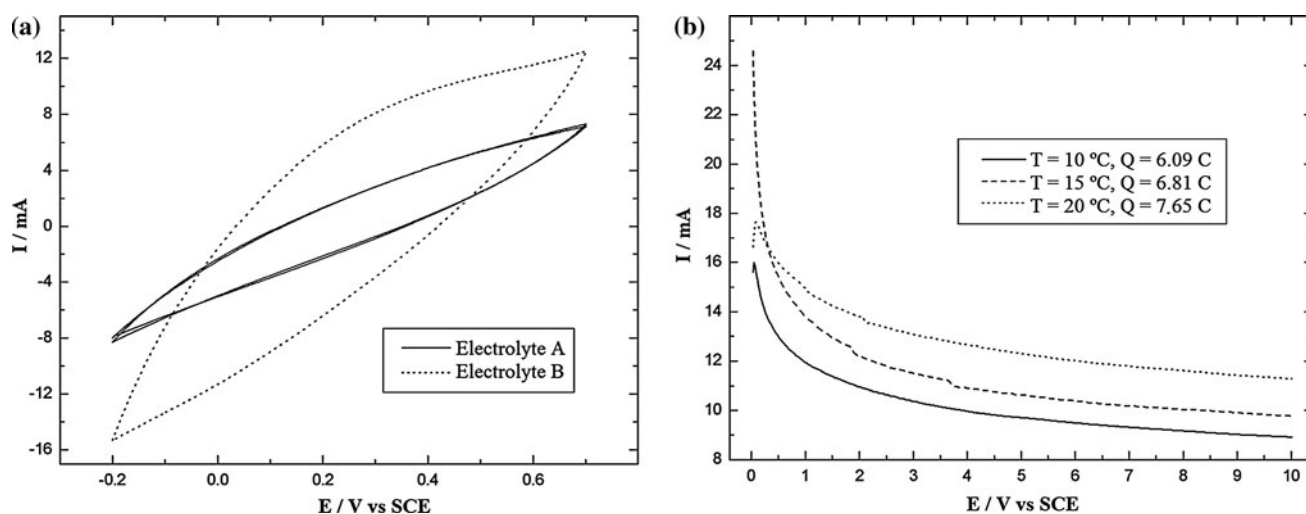


Fig. 2 a SS/PPy electrochemical response in A 25 mmol L⁻¹ Na₂SO₄, pH 1.5, B 50 mmol L⁻¹ Na₂SO₄, pH 1.5. $\nu = 50$ mV s⁻¹. b Temperature effect on electro-polymerization by PM at 0.980 V. SS/50 mmol L⁻¹ Py + 50 mmol L⁻¹ Na₂SO₄, pH 1.5

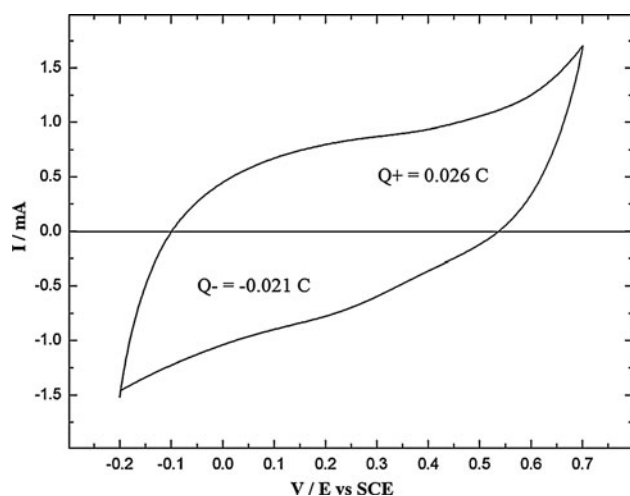


Fig. 3 Charge associated to arsenic extraction by CV, SS/PPy/100 ppm As(V) + 50 mmol L⁻¹ Na₂SO₄, pH 1.5. $\nu = 50$ mV s⁻¹

used, applying 0.700 V as doping potential, and -0.200 V as undoping one in a solution containing only the supporting electrolyte (50 mmol L⁻¹ Na₂SO₄, pH 1.5) to obtain the EC represented in Scheme 1 [24, 25].

All doping experiments were performed applying the potential for 60 s. Subsequently, to determine the optimal undoping time for the quantitative release of arsenate ion, three comparative extractions, for 40, 60, and 80 s, at the selected undoping potential, were conducted. The results showed that a time shorter than the doping time would not be appropriate, because a charge decrease was obtained when performing the undoping, probably because not all arsenate species had been released.

On the other hand, when comparing 60 and 80 s undoping times, an increase in extraction charge was observed and,

consequently, a greater release of arsenate ions. However, between these two times no significant advantages were appreciated and, thus, 60/60 s doping/undoping processes were utilized. The respective voltammetric profile is depicted in Fig. 3.

3.3.2 Extraction time effect on doping/undoping

The effect of extraction time was evaluated for 10 and 20 min EC. For both, the doping process was accomplished using a 148.40 ppm As(V) solution. The extracted As(V) was then removed by undoping in a supporting electrolyte solution utilizing another electrochemical cell. Twelve and eight EC for 10 and 20 min, respectively, with doping/undoping of 120 min and $8 \times 20 = 160$ min, were conducted. If the absolute charges obtained in Fig. 4a and b are compared, an EC increase, as expected, brings about a doping charge decrease owing to some electro-activity loss by the inclusion of As(V) ions. By contrast, undoping causes a charge increase [26].

If the doping process were plotted separately for both EC times (Fig. 4c, d) it could be more clearly seen that as the specific concentration intervals varies, the mechanism of action of SS/PPy and its SC change [27]. In the first slope, in both Fig. 4c and d, when concentration increases, it is expected that the extraction process depends on both the applied potential and ions diffusion from the bulk solution to the electrode/solution interface and on the diffusion of the same ions into the polymeric matrix. Nevertheless, as concentration decreases, the extent to which these factors are affected varies. Diffusion into the matrix becomes the predominant contribution. This would explain slope variation and decrease as the measurement takes place. Figure 4b and c also shows that extraction efficiency

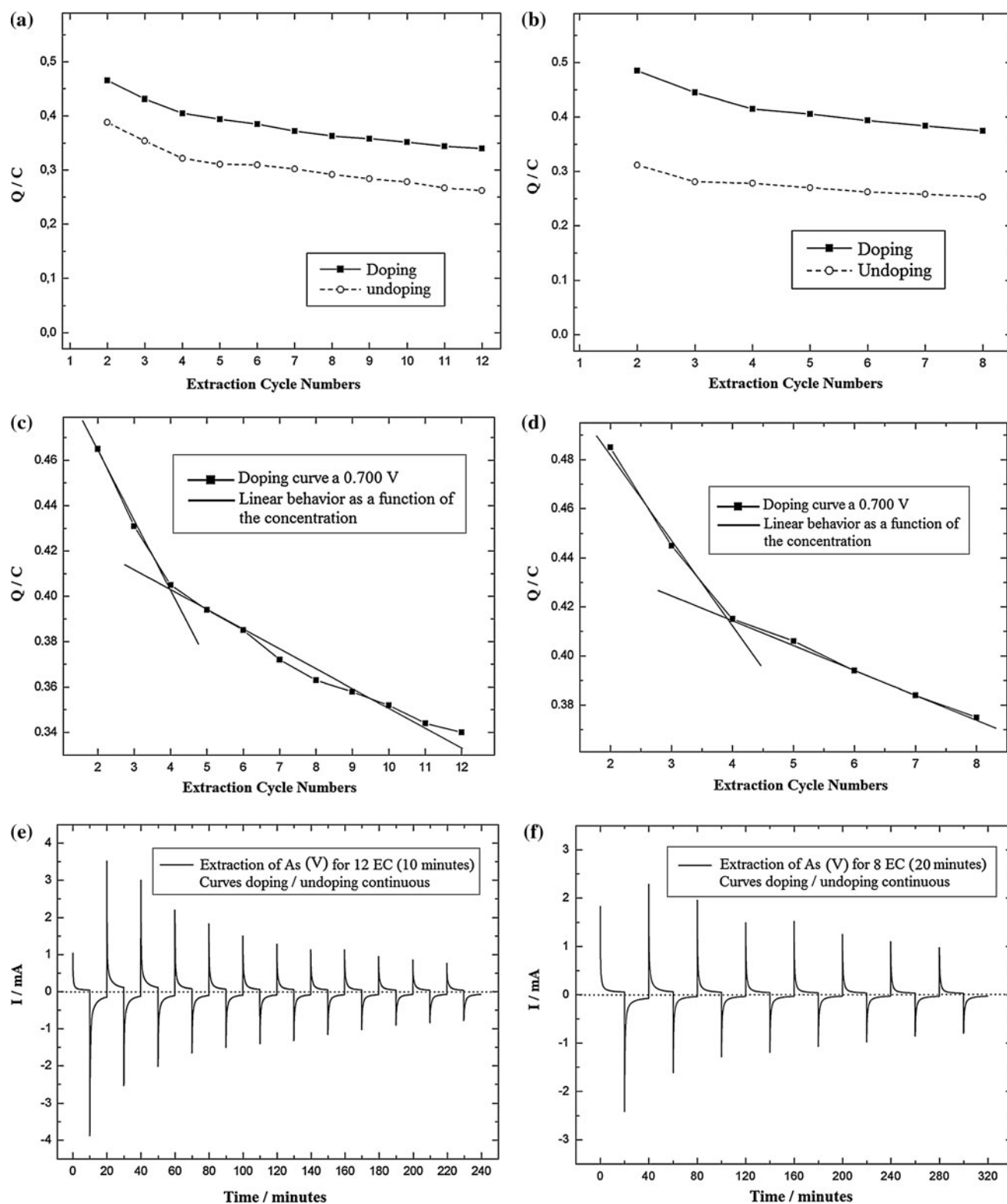


Fig. 4 **a, b** Absolute magnitudes of As(V) extraction data with SS/PPy by EC of 10 and 20 min, using PM. *Doping interface*: SS/PPy/148.40 ppm As(V) + 50 mmol L⁻¹ Na₂SO₄, pH 1.5. *Undoping interface*: SS/PPy 50 mmol L⁻¹, Na₂SO₄, pH 1.5. **c, d** Behavior

of doping with SS/PPy during As(V) removal by 10 and 20 min EC. **e, f** i/t transients for 12 consecutive EC of 10 min each and 8 EC of 20 min each

Table 4 Results obtained for calculating EC actual efficiency using 10 and 20 min extraction times

Time EC	10 min	20 min
EC number	12	6
Total time (min)	120	120
Initial doping solution (ppm)	135.75	135.75
Final doping solution (ppm)	26.64	24.18
Undoping solution (ppm)	104.99	96.94
Loss (ppm)	4.12	14.66

decreases as the time varies from 10 to 20 min. If a comparison of the charges associated with doping/undoping processes during the same period of time for total extraction is conducted, it will be seen that for 12 EC, 10 min each, the theoretical extraction percentage is 84.97 %, instead for 20 EC, 8 min each, the obtained percentage was 71.39 %. Hence, it is evident that longer cycle times do not improve the total removal efficiency. However, it seems that extraction efficiency improves when a greater number of shorter time cycles are utilized. Figure 4e and f exhibit plots of successive EC in order to compare what happens during the extraction potential application. In both plots the currents converge, as occurs with the charges. On the other hand, studies concerning to the proportionality of the maxima of each EC revealed lack of linearity. Furthermore, it is observed that for 20 min EC the current converges to zero more rapidly than for the 10 min EC. Consequently, the maximum SC of the SS/PPy film would be achieved by applying the potential for longer times, but this implies that the extraction efficiency decreases. Therefore, to obtain the best results, both factors need to be appropriately conjugated.

3.3.3 EC actual efficiency for 10 and 20 min extraction time

To calculate the real efficiency, a 135.75 ppm As(V) solution, under the already stated doping/undoping conditions, was initially utilized. A total extraction time of 120 min is used for both assays.

Table 4 revealed that the number of cycles, and not the disturbance application time, contributes more to As(V) removal, as justified for EC 6 since the final undoping solution is considerably lower. Thus, although extracts more, the percentage recovery in this case is lower than when using EC 12. Consequently, it would be advisable, to achieve higher As(V) recovery rates, to carry out a greater number of 10 min EC. Another way to achieve this goal would be increasing the SS electrode geometric area and, thereupon, that of SS/PPy. This way, the contact area increases even further as a consequence of polymer porosity and thus the amount of material by extracting cycle increases as well, i.e., a lesser number of ECs would afford higher extracting efficiency.

3.3.4 Diffusion effect on SS/PPy electrode

The effect of diffusion on the modified electrode was evaluated to determine if some kind of bias in the electrochemical response exists when As(V) extraction and recovery assays are carried out [28]. To this purpose, the diffusional effect was studied at a SS/PPy-modified electrode. The device was left for 24 h into a 135.75 ppm As(V) stirred solution. Then, a -0.200 V undoping perturbation was applied for 1 h in a supporting electrolyte solution ($50 \text{ mmol L}^{-1} \text{ Na}_2\text{SO}_4$, pH 1.5). Subsequently, the arsenic concentration was quantified. The result was 0.12 ppm As(V), i.e., a 0.09 % of the initial concentration had diffused into the polymeric matrix. This value increased with increasing initial concentration of the solution. However, is still negligible compared to 71.39 % of actual extraction determined in Sect. 3.3.3.

3.3.5 Effect of arsenic concentration on SS/PPy

The effect of As concentration was assessed by CV employing 50, 100, and 500 ppm As(V) solutions. A maximum current vs As(V) concentration plot showed a linear relationship. Linear regression analysis gave the equation $I \text{ (mA)} = 5.10 \times 10^{-6} [\text{As(V)}] \text{ (ppm)} + 0.00962$ and correlation coefficient $r = 0.999$. This result is very important regarding to the projection of the modified electrode for designing an arsenic sensor based on the system used herein.

4 Conclusions

The fabrication of an SS/PPy-modified electrode was successfully optimized to be used as As(V) extractant. The optimal conditions found in this study were doping/undoping disturbances at 0.700 and -0.200 V, respectively. These potentials enabled generating greater amount of charge, making the process more reversible and reproducible without modifying the conjugated π system.

As for factors affecting the measurement at the electrode, it is possible to conclude that, although some electroactivity loss exists, this is not ascribable to changes in the polymeric matrix, but rather to anions retention provided by the supporting electrolyte. The response of the SS/PPy-modified electrode was also found to be highly sensitive to temperature and ionic species present in the cell, showing, for instance, a tendency to decrease the thickness of the coating as temperature increases.

With regard to SC, it was found that at high As(V) concentration, the extraction depends on the applied potential and ions diffusion from the bulk of the solution to the electrode/solution interface and their diffusion into the polymeric matrix. However, when concentration decreases,

the extent to which these factors affect varies; contribution of diffusion into the matrix being predominant.

The theoretical and actual percentage of arsenic removal employing SS/PPy under optimized conditions of electro-synthesis and extraction, are of similar magnitude. Real and theoretical extraction percentage for 10 min EC was, respectively, 77.34 and 84.97 %. As for 20 min EC, the actual and theoretical extraction percentage was 70.71 and 71.39 %, respectively.

Finally, as the doping/undoping charge ratio and arsenic concentration exhibited a linear relationship, it is possible to propose the herein optimized electrode as a prospective arsenic amperometric sensor, at least between 50 and 500 ppm.

Thus, applications of this SS/PPy-modified electrode are promising. First, it was verified that As(V) extraction efficiency can be optimized as a function of the variables described herein. Hence, in the next stage of this survey its selectivity will be assessed. Second, it was found that utilizing the same SS/PPy device, an As sensor may be developed. To this purpose, in addition to selectivity, other analytical parameters such as detection limit, sensitivity, response time, etc. need to be established.

Acknowledgments The authors acknowledge financial support from FONDECYT through project 1100055.

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